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PHENOLIC POLYMER USED FOR ABLATIVE COMPOSITES

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

[Analysis of the decomposition characteristics of a phenol-formaldehyde polymer by differential thermal analysis, gas chromatography, and elemental analysis has shown the overall process to consist of a series of complex reactions ranging from low-temperature crosslinking](curing)[to a high-temperature reaction which results in a carbon char.] The energy absorption through decomposition was found to be 293 kJ/kg over the temperature range between 350° C and 850° C. The efflux of volatile products corresponding to this decomposition consisted of components ranging in molecular weight from hydrogen to dimethylphenol (2 to 122). Fifty percent of the total moles identified were hydrogen and 23.4 percent and 10 percent were found to be water and methane, respectively. Analysis of the residue showed that the carbon char appeared over the 400° C to 850° C temperature range concurrent with the formation of volatile oxidized products. The char at 850° C was found to be 92.6 percent carbon, 0.9 percent hydrogen, and 6.5 percent oxygen.

INTRODUCTION

The optimum use of ablation materials as a heat-absorbing mechanism for reentry vehicles requires a complete understanding of all processes, physical and chemical, which contribute to the functioning of the material. The Langley Research Center has embarked on a program designed to provide a basic understanding of and provide experimental data on the individual heat-accommodating processes of these materials.

The purpose of this paper is to report the results of one phase of this program. This phase provides experimental data on the characteristics of thermal decomposition of phenolic by studying the reactions involved, the volatile products of these reactions, and the changes which occur in the char as a result of these reactions.

Phenolics have been found to be an effective ingredient in composite charring ablation heat-shield materials. The effectiveness of this material is due in part to the carbonaceous residue which results from decomposition. As a result, there have been many investigations into the performance of phenolic and phenolic composites in simulated reentry environments. (For example, see refs. 1, 2, and 3.) From these investigations

it has been possible to deduce some valuable information on the overall characteristics of thermal decomposition which occurs in the pyrolysis zone. Specific details of the decomposition, such as heat of pyrolysis, pyrolysis temperatures, composition of the decomposition gases, etc., which are needed for complete evaluation, are available only through analytical techniques designed to determine such quantities. Although extensive work in references 4, 5, and 6 has produced data on the thermal decomposition of phenolic, these investigations were undertaken by using, in most cases, different resins (prepared under controlled laboratory conditions) than are normally used as ablation material components. The phenolics of these investigations therefore represent quite different materials from those actually fabricated in large quantities for evaluation as reentry ablation materials.

In this report, the characteristics of thermal decomposition are given for a phenolic which is used as a charring component in ablation materials. This material was produced under conditions similar to those used for fabrication of the arc-jet test models of references 1, 2, and 3. Characterization of the material was accomplished through use of several analytical techniques. Differential thermal analysis (DTA) provided information on the character of the pyrolysis reactions whereas gas chromatography was used to determine the composition and quantities of the products evolved through these reactions. In conjunction with the DTA, effluent gas analysis (EGA) yielded data on the total gas evolution and enabled the DTA data to be correlated with the gas chromatograph and mass loss data. Analysis of the residue and char of decomposition was obtained by elemental analysis. Through these techniques (differential thermal analysis, effluent gas analysis, gas chromatography, and elemental analysis), an extensive characterization of the decomposition of phenolic was obtained.

The units used for the physical quantities defined in this paper are given in the International System of Units (SI). Reference 7 presents factors relating the International System with other frequently used systems of units.

MATERIAL

The material characterized in this investigation was a phenol-formaldehyde resin of the Union Carbide Corporation (type designation, BRP 5549). The "B" stage or novolac-type resin premixed with hexamethylenetetramine is supplied by the manufacturer. When used with composite materials, such as the case in the evaluation test of references 1, 2, and 3, the resin-hexamethylenetetramine mixture is evenly mixed with the other components of the composite before molding. The entire composition is molded by using the standard cure procedures:

Cure:

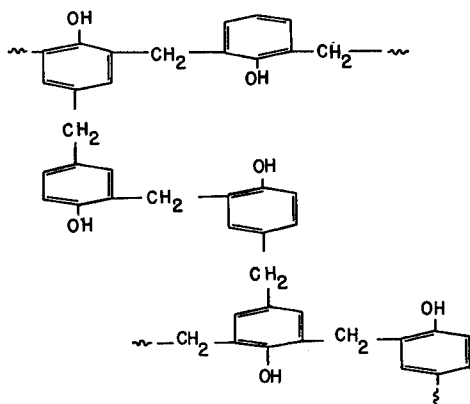
- (1) Pull vacuum of 670 N/m^2 (5 torr) or greater for 0.5 hour before heating and maintain throughout cure.
- (2) Heat resin from ambient to 165°C at approximately 210°C/hour .
- (3) Hold at 165°C for 1 hour.
- (4) Cool to ambient temperature.

Post cure (in an air oven):

- (1) Ambient to 38°C and hold for 1 hour.
- (2) Rise from 38°C to 94°C at 5.6°C/hour and hold for 10 hours.
- (3) Rise from 94°C to 116°C at 2.8°C/hour and hold for 10 hours.
- (4) Rise from 116°C to 149°C at 2.8°C/hour and hold for 10 hours.
- (5) Cool to ambient at 14°C/hour .

In order to obtain as close as possible the same degree of cure as the phenolic in the composite materials, the phenolic resin for this investigation was also carried through these same cycles. However, because of the absence of other materials, the phenolic specimen was molded considerably smaller than the usual arc-jet ablation model in an attempt to obtain a uniform degree of cure throughout the specimen. The phenolic specimen material was molded in a thin disk 2.5 cm thick and 10 cm in diameter.

The novolac resin was formed with a deficiency of formaldehyde and subsequently mixed with the hexamethylenetetramine. To cure the resin to an infusible, insoluble, highly crosslinked polymer, the resin-hexamethylenetetramine mixture is heated. The formaldehyde which is needed for the completion of the condensation and crosslinking reaction results from breakdown of the hexamethylenetetramine. Ammonia is also a product of this breakdown and serves as the catalyst. The polymer formed is a hard brittle material similar in structure to the following:



After the completion of the cure—post-cure cycles, the specimen was placed in a vacuum oven to prevent absorption of moisture while awaiting testing. The molded specimens remained in the oven at 90° C for a minimum of 200 hours before analytical testing.

The individual specimen configuration varied with each technique used; however, all specimens were taken from approximately the same location in the molded disk in order to obtain similar degrees of cure. Each individual specimen was cut or filed from the molded disk at the time of testing; therefore, it did not remain as a powder or small piece in the oven so that further individual curing could occur. The specimen for the DTA-EGA technique consisted of approximately 60 mg of filings from the molded disk whereas the gas chromatograph pyrolysis samples were solid rectangular slugs having a mass of approximately 7 mg.

ANALYTICAL TECHNIQUES AND TEST PROCEDURES

Differential Thermal Analysis

When heated to a sufficiently high temperature, virtually all materials will undergo some physical or chemical changes, ranging from simple phase changes to complete decomposition. During these physical and chemical changes there will be measurable changes in the total heat content of the material. To establish where and if a reaction did occur, it is only necessary to compare continuously the total heat content of the specimen material with that of an inert reference material while both are heated in the same environment through a temperature range of interest.

Experimentally, in the differential thermal analysis (DTA) apparatus, the temperature difference between a specimen material and an inert reference material is obtained by a differential thermocouple. As the reactions occur, the specimen temperature will either lead the reference material temperature and indicate an exothermal reaction or lag the reference material temperature and thus indicate an endothermal reaction. When no reaction is occurring in the specimen, the difference in temperature ΔT is zero; thus, a straight horizontal line would be observed on the thermogram (plot of ΔT as a function of temperature). The various endothermal and exothermal reactions through which the material passes are thus displayed as downward or upward peaks on the thermogram. With a linear heating rate, the area under these peaks is proportional to the quantity of heat involved in the reaction from which the peak results. Calibration of the apparatus is easily accomplished by utilizing the known heat of fusion of certain inorganic and organic compounds. A more complete discussion of differential thermal analysis, its methods and techniques, may be found in reference 8.

The particular apparatus used in this investigation is described completely in reference 9. Basically, it consists of a controlled pressure and controlled atmosphere DTA

apparatus of a commercial source. The specimen materials are heated in a small inconel cup situated on the differential thermocouple inside the inconel block specimen holder. The sample holder, provided with gas injection ports at its base, allows for a continuous flow (helium) over the specimen and reference materials. The entire specimen holder was heated by a resistance furnace and controlled by a thermocouple situated between the beads of the differential thermocouple in the inconel block. The resulting thermogram was a plot of differential temperature as a function of block temperature. After flowing over the specimen material, where any evolved decomposition products are combined with the helium gas flow, the combination of helium and these products are passed through a thermal conductivity detector where differences between it and the injected gas (helium) are noted. The output of the thermal conductivity detector is also plotted as a function of block temperature (EGA thermogram). The sample holder is heated at 10° C per minute from ambient to 900° C and the differences in temperature produced between a specimen of phenolic and an aluminum oxide reference material are recorded as a function of increasing temperature.

Elemental Analysis

The residues and char to be analyzed by elemental analysis were those obtained by heating the polymer to the desired temperature in the DTA sample holder. The individual specimens were heated at 10° C per minute in a helium atmosphere from ambient to the analysis temperature. Upon reaching the desired temperature, the furnace was immediately removed and the specimen holder cooled to ambient, by forced air cooling, to prevent further decomposition. During this cooling process, the specimen remained in the dry helium atmosphere. Once cooled, the mass loss was determined and the specimen placed in moisture proof containers to await elemental analysis. The elemental composition was determined by a method based on burning the sample in 100 percent oxygen at 900° C. The products of this combustion, water and carbon dioxide for the carbon-hydrogen determination, were caught and weighed in absorption tubes.

The nitrogen determination was based on pyrolysis of the sample in a carbon dioxide atmosphere inside a quartz tube packed with zones of copper oxide and reduced copper at 700° C. The nitrogen was collected and measured over a potassium hydroxide (KOH) solution in an azotometer.

Gas Chromatography

Gas chromatography is an analytical technique used to separate a mixture of gases into its various constituents. Fractionation of the mixture is accomplished by means of a liquid-coated solid support. The coated support is packed into a long column into which the mixture of gases is injected and carried through the column by a carrier gas whose characteristics are widely different from those of the injected gases. The fractionation

process, occurring along the length of the column, consists of a multiple partition between the liquid and gas phases. The time required to pass through the column for a particular species (retention time) depends upon both its vapor pressure and solubility in the immobile liquid. Therefore, the liquid phase is normally varied to obtain the best fractionation of a complex mixture of gases.

As the fractionated species of a gas mixture are eluted from the column, they pass through a detector which notes the difference in thermal conductivity of the carrier gas as a product appears. The output of the thermal conductivity detector, in conjunction with a Wheatstone bridge, generates an electrical signal proportional to the amount of component in the carrier gas. The signal of the thermal conductivity detector recorded as a function of time is called a chromatogram. A more complete description of the principles involved in gas chromatography may be found in reference 10.

The experimental apparatus used in this investigation was a commercially available programmed high-temperature gas chromatograph. Three columns, each 6.35-mm diameter, were used with this apparatus. A 3-meter column with a 10-percent Carbowax 20 M coating on a Teflon 6 substrate was used to determine the quantity of water evolved over the temperature range from ambient to 900° C. Figure 1 shows a typical chromatogram

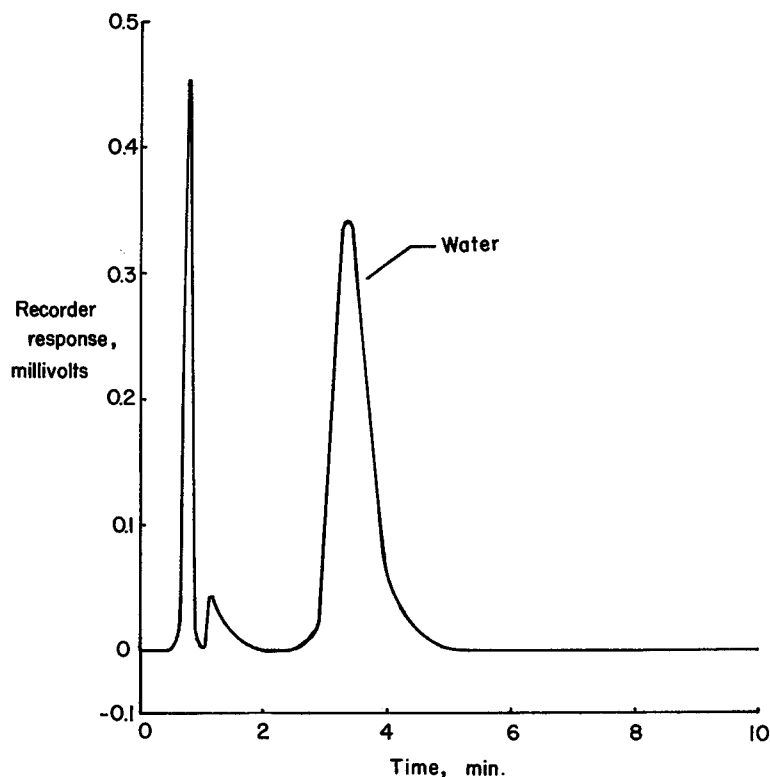


Figure 1.- Pyrolysis chromatogram of phenolic at 450° C.

obtained by using this column. In particular, the chromatogram shows the pyrolysis of a 7-mg phenolic specimen at 450° C. The column was held isothermal at 75° C throughout the analysis. The water peak is indicated on the chromatogram and was identified by its retention time. The second column used was a 3-meter molecular sieve 5A column. The column was held isothermal at 100° C for 6 minutes before programing at 2.9° C per minute through 175° C. A typical chromatogram is shown in figure 2, where the pyrolysis occurred at 650° C. Through use of this column, the noncondensable gases, hydrogen, methane, carbon monoxide, and carbon dioxide, were separated. The column conditions are shown on the chromatogram in this figure.

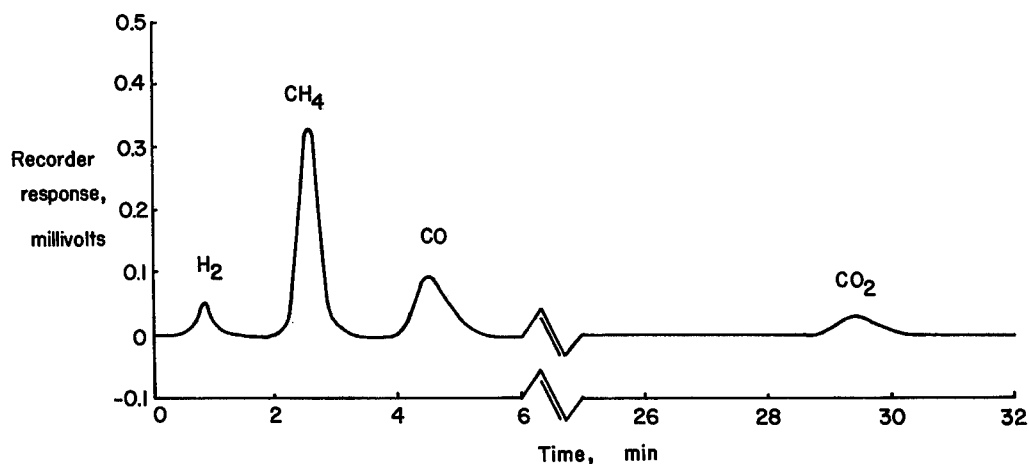


Figure 2.- Pyrolysis chromatogram of phenolic at 650° C.

A 3.4-meter column with a 10-percent Carbowax 1500 on firebrick was the third column used. A chromatogram resulting from the use of this column is shown in figure 3 for a typical phenolic pyrolysis at 600° C. The column conditions consisted of holding isothermally at 50° C for 6 minutes before programing at 5.6° C per minute to 200° C and then holding until the analysis was complete. The overall analysis was complete in 56 minutes. The high molecular weight components of pyrolysis, benzene, toluene, phenol, and xylenol, were identified through use of this column.

The determinations of the quantities involved in each chromatogram were accomplished through calibration of the gas chromatograph detector by a method similar to that used in reference 11. This procedure consisted of obtaining calibration factors for each identified product, such that the area under each chromatograph peak could be converted to the quantity of evolved product. Identification of the pyrolysis products in each chromatogram was made by comparison of the retention times of the observed peaks with those of the suspected compounds by successive injections of the pure compound.

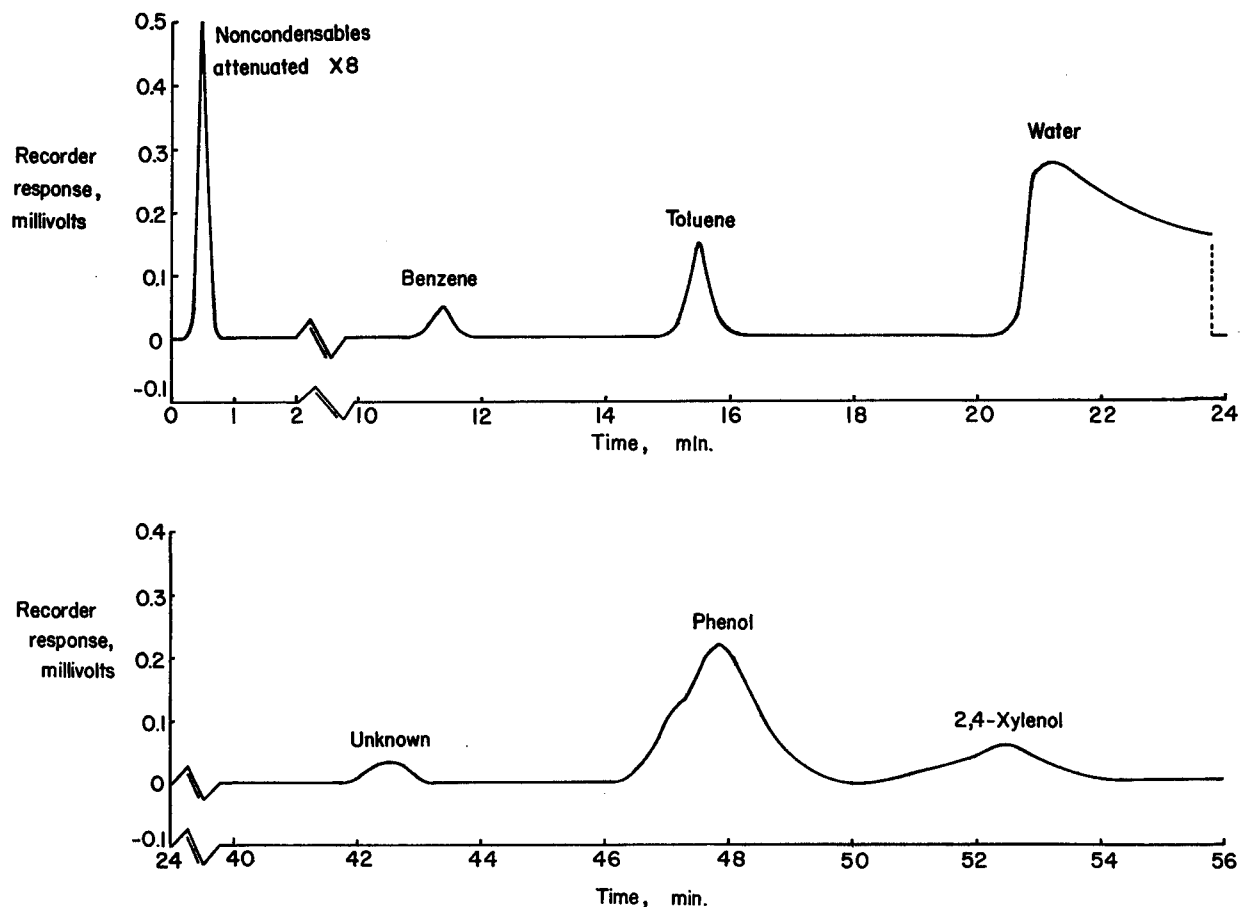


Figure 3.- Pyrolysis chromatogram of phenolic at 600° C.

Pyrolysis Gas Chromatography

The phenolic specimens were pyrolyzed in the entrance port of the gas chromatograph by means of a standard commercial type pyrolyzer which employs a platinum coil as a heater. The phenolic specimen was a solid rectangular piece with a mass of approximately 7 mg and for pyrolysis, was wedged tightly into the center of the platinum coil. The pyrolysis of the phenolic specimen was accomplished by heating the specimen from the chromatograph entrance temperature to the test temperature over a 10-second interval. After the specimen was cooled to entrance temperature, the test temperature was increased by 50° C and the process repeated.

The pyrolysis temperature was determined by a method similar to that used in reference 12. The procedure utilized involved using the known melting point of several polymers and several inorganic salts to determine a relationship between voltage input to the pyrolyzer coil and the apparent specimen temperature. The sizes of the calibration materials used were maintained approximately equal to that of the phenolic specimen.

Because coil aging could affect this calibration, a new coil was used after each series of runs. (A series consisted of pyrolysis of a phenolic specimen at 50° C increments from 100° C to 1000° C.) Variation in pyrolysis temperature calibration was found to be negligible with the use of this procedure.

ANALYSIS AND DISCUSSION OF RESULTS

Analysis of Results

The differential thermal analysis (DTA) thermogram in figure 4 shows the sequence of reactions involved as the cured—post-cured phenolic polymer is heated from ambient to 900° C in a helium atmosphere at 10° C per minute. The exothermal peaks, extending upward from the base line ($\Delta T = 0$), and the endothermal peaks, extending downward from the base line, are shown with the energy associated with each of the major reactions marked above or below the reaction peak. The thermogram is observed to consist of two basic sections: the first, covering the temperature interval from ambient to 350° C (section A), involves only a small quantity of energy relative to the second (section B) which covers the remainder of the thermogram from 350° C to 900° C. Section A appears to involve two separate processes, one endothermal and the other exothermal. The endothermal process, whose peak is at 100° C, is considerably smaller in size than any other single reaction or process observed to occur over the temperature range investigated. In this temperature range, the effluent gas analysis (EGA) thermogram in figure 5, obtained simultaneously with the DTA results, shows an addition to the carrier gas to have occurred at this temperature. The EGA thermogram, a plot of thermal conductivity detector output as a function of increasing temperature, gives some idea as to the total volume of gas being evolved during the reaction. However, identification of the

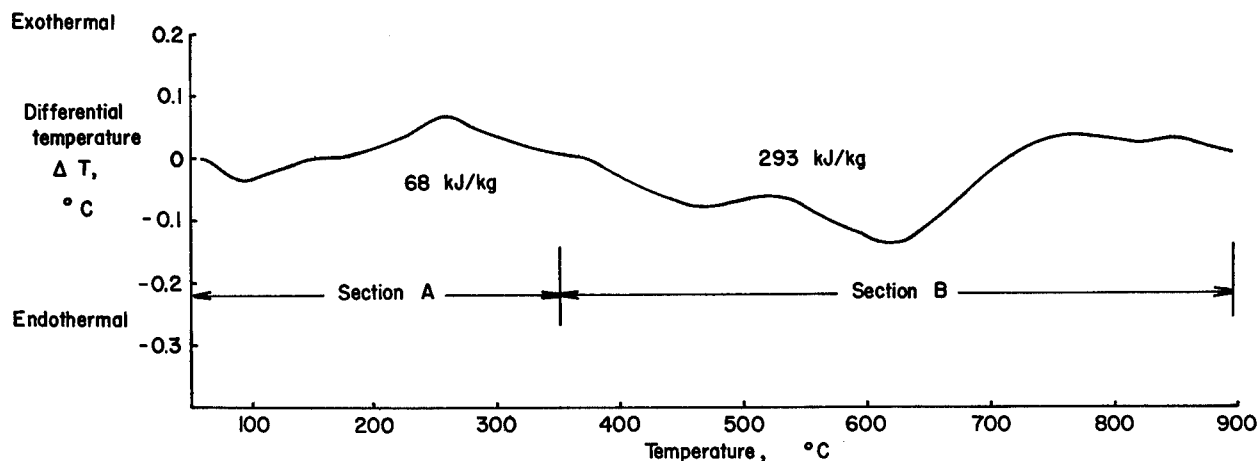


Figure 4.- Differential thermal analysis thermogram of phenolic.

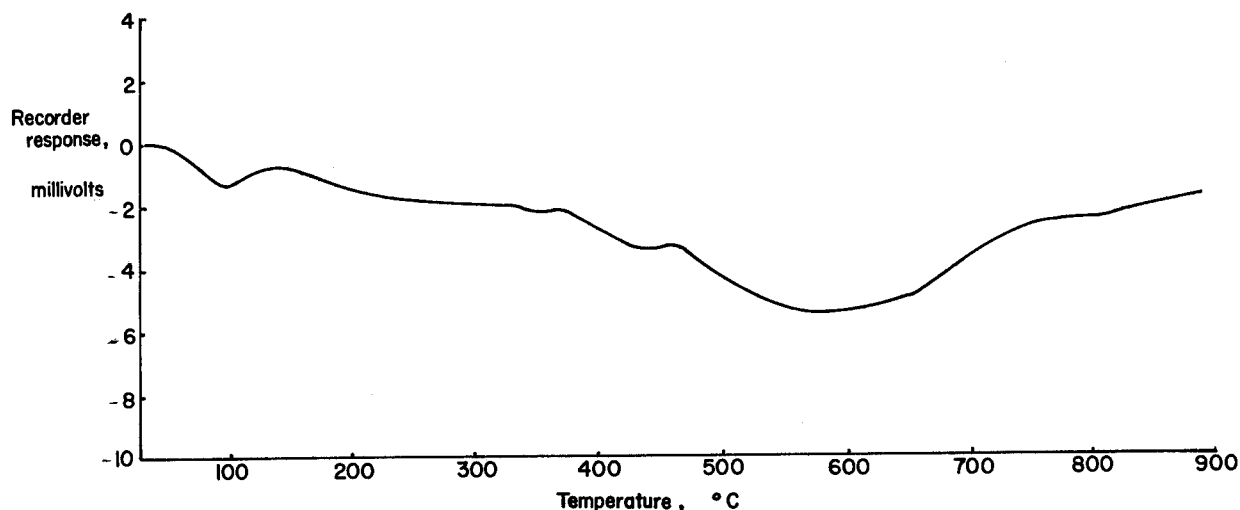


Figure 5.- Effluent gas analysis thermogram of phenolic.

evolved component, which was determined to be water, was obtained by heating the specimen in the gas chromatograph and separating the evolved products. The results of identification of the evolved products from the endothermic process in section A and those observed over the entire investigated temperature range (sections A and B) are shown in table I. This table shows the products identified and the quantity of each for 50° C temperature intervals from 100° C to 1000° C. The quantity of each component present is normalized with respect to the total moles observed and therefore does not reflect any lost species. At the base of each column the observed quantities at each pyrolysis temperature are summed to give the total of each component over the investigated temperature range.

TABLE I.- PRODUCT DISTRIBUTION FROM DECOMPOSITION OF PHENOLIC

| Temperature, °C | Total moles observed, percent | | | | | | | | |
|--------------------|-------------------------------|------|-------------------------------|-------------------------------|-----------------------------------|---|-----------------|------------------|----------------|
| | CO ₂ | CO | C ₆ H ₆ | C ₇ H ₈ | C ₆ H ₅ -OH | (CH ₃) ₂ C ₆ H ₃ -OH | CH ₄ | H ₂ O | H ₂ |
| 100 | | | | | | | | 1.47 | |
| 150 | | | | | | | | .75 | |
| 200 | | | | | | | | .48 | |
| 250 | | | | | | | | .57 | |
| 300 | | | | | | | | 1.28 | |
| 350 | | | | | | | | 3.44 | |
| 400 | | | | | 0.46 | 0.13 | 0.05 | 3.44 | |
| 450 | | 0.21 | | | .81 | .25 | .15 | 5.42 | 0.76 |
| 500 | 0.09 | .44 | 0.02 | 0.08 | 2.72 | .75 | .75 | 3.35 | 1.47 |
| 550 | .11 | .87 | .06 | .13 | 1.62 | .38 | 1.29 | 2.44 | 2.18 |
| 600 | .32 | 1.30 | .06 | .05 | .79 | .14 | 2.61 | .40 | 3.65 |
| 650 | .51 | 1.19 | .03 | .04 | .44 | .10 | 2.35 | .26 | 5.17 |
| 700 | .26 | .77 | | .01 | .21 | .05 | 1.32 | .13 | 5.88 |
| 750 | .17 | .54 | | | .09 | | .83 | | 6.64 |
| 800 | .11 | .26 | | | | | .40 | | 7.35 |
| 850 | | .20 | | | | | .20 | | 5.88 |
| 900 | | | | | | | .08 | | 4.50 |
| 950 | | | | | | | | | 3.65 |
| 1000 | | | | | | | | | 2.94 |
| Total | 1.6 | 5.5 | 0.2 | 0.3 | 7.1 | 1.8 | 10.0 | 23.4 | 50.1 |

The results in table I are plotted in figures 6 and 7 and can be compared with the DTA and EGA results of figures 4 and 5. Figure 6 shows the evolution of water, methane, and hydrogen, and figure 7 exhibits the evolution characteristics of phenol, xlenol, and carbon monoxide. Carbon dioxide, benzene, and toluene, evolved in small quantities, were not plotted. From these results, it is apparent that water was the only product identified through the endothermic range of section A. Although the polymer was molded, post-cured, and subsequently retained thereafter in a vacuum oven, it appears that water had been sufficiently trapped during molding, to prevent desorption through the standard post-cure procedures or drying in the vacuum oven. With an extended post cure of 225° C for 24 hours, however, it was possible to eliminate the trapped water evolved at low temperatures (100° C to 225° C). The effect of an extended post cure upon the production of water is shown in figure 8. Only that portion of the curve below 300° C was observed to change with the extended cure. The effect of this extended cure upon the evolution of the remaining products of table I was not determined.

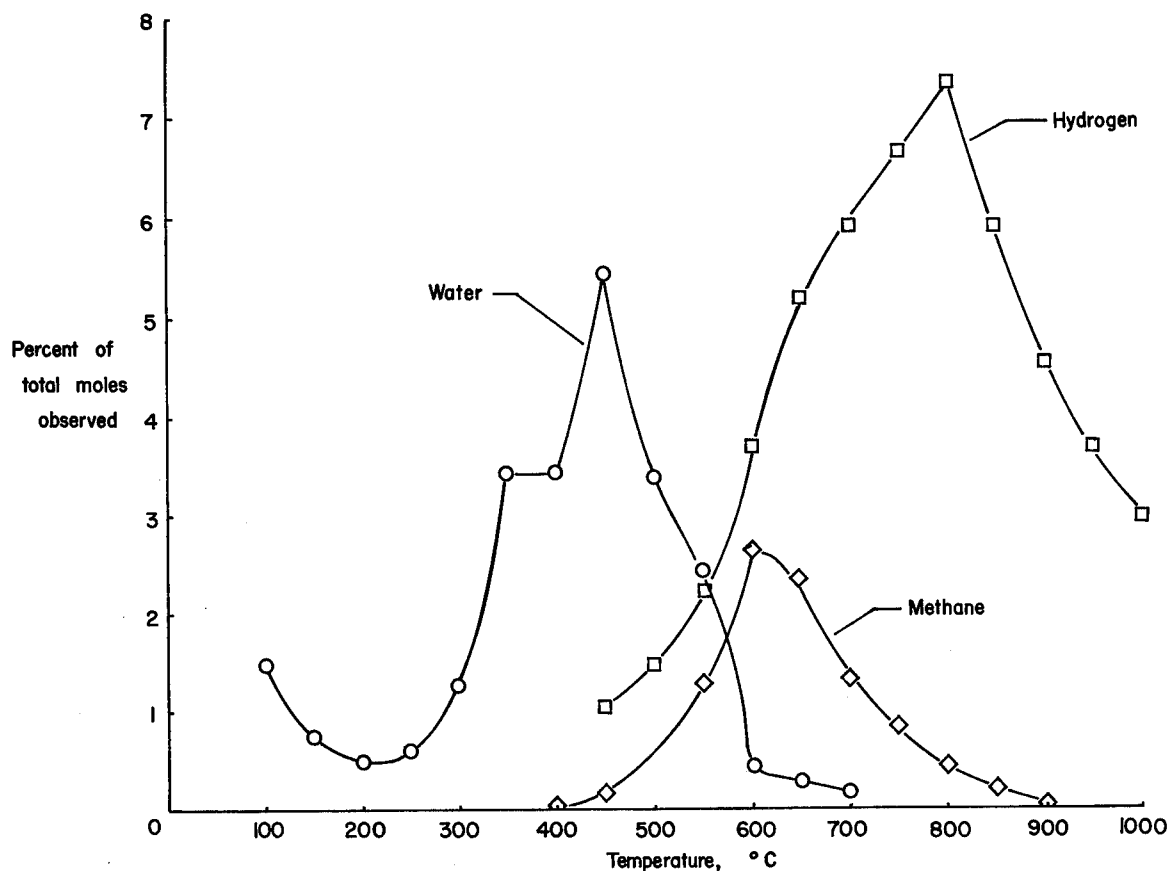


Figure 6.- Product distribution from decomposition of phenolic. Evaluation of water, methane, and hydrogen.

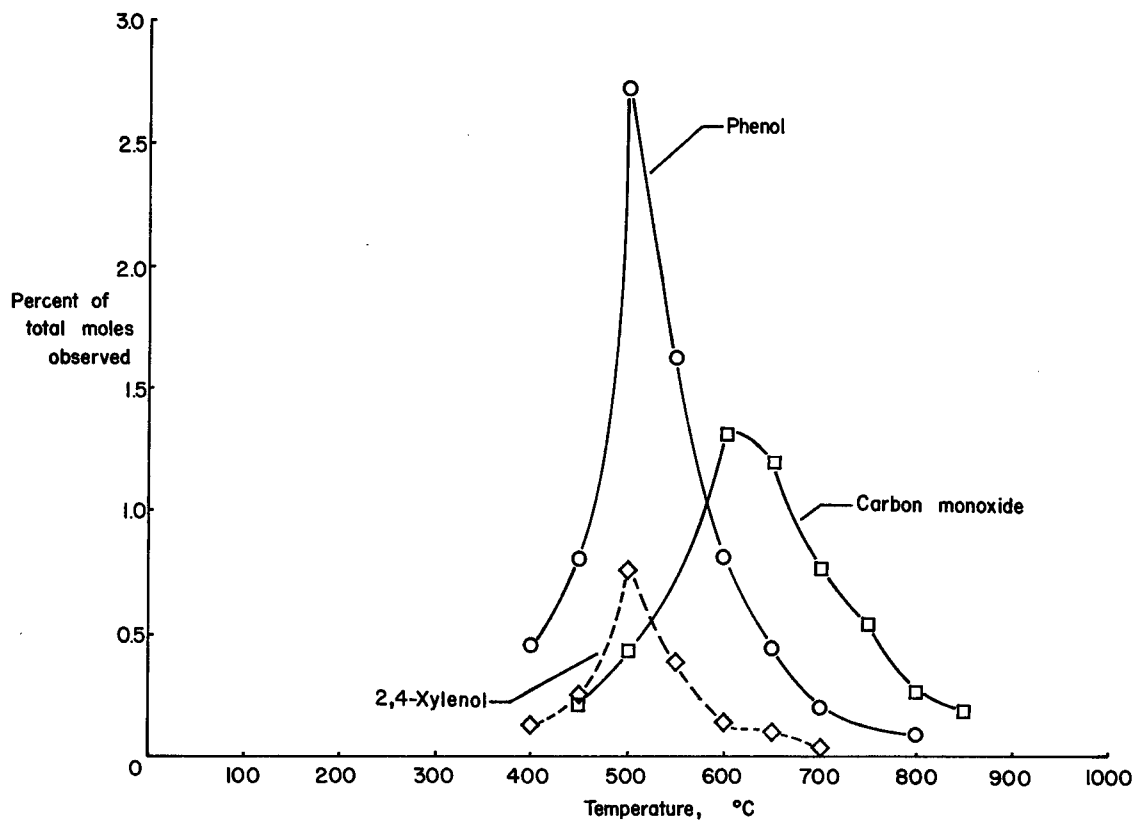


Figure 7.- Product distribution from decomposition of phenolic. Evaluation of 2,4-xyleneol, carbon monoxide, and phenol.

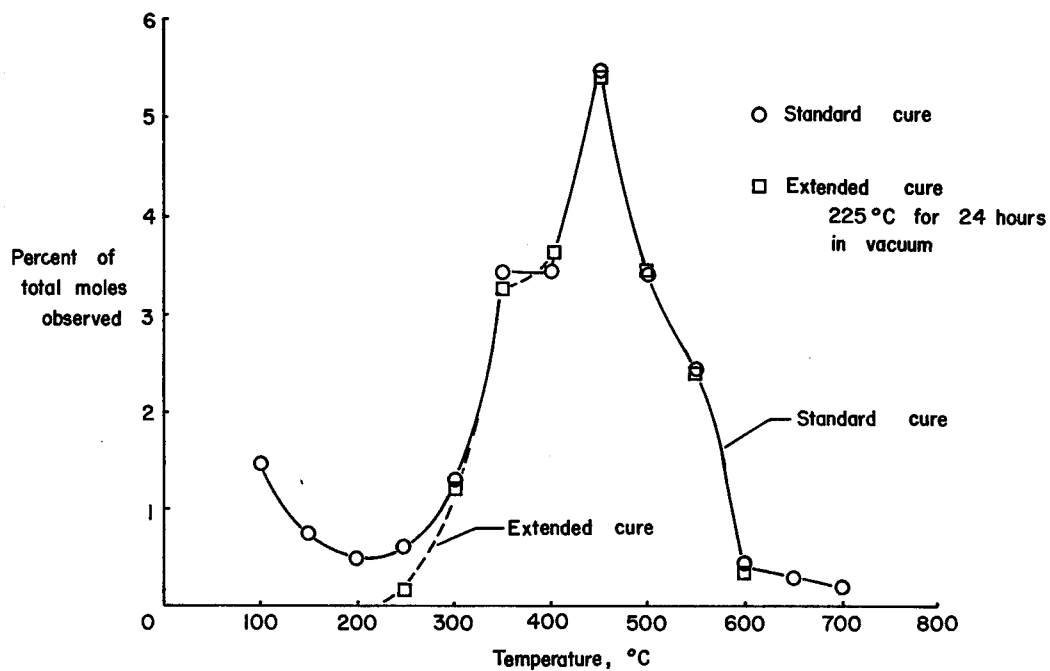


Figure 8.- Effect of extended cure on the production of water from decomposition of phenolic.

Although species which indicate entrapment of other components were not specifically identified, the results of elemental analysis of the starting polymer (table II) clearly indicate this situation to exist, as will be shown later. Table II lists the percent by mass of carbon, hydrogen, and nitrogen in the polymer before heating in the DTA apparatus. It should be noted that the elemental analysis only identifies the elements carbon, hydrogen, and nitrogen. The percentage remaining was assumed to be oxygen as a result of finding the uncured resin to have an insignificant ash content. (The actual ash content was determined, from unpublished data of an NASA contractor, to be 0.04 percent.) Also shown in this table are the results of analysis of the residue as the polymer was heated from ambient to 850° C (according to the procedure outlined previously) and the mass loss which accompanied these changes.

TABLE II.- RESULTS OF ELEMENTAL ANALYSIS

| Temperature, °C | Percent by mass | | | | Mass fraction |
|--------------------|-----------------|----------|----------|--------|---------------|
| | Carbon | Hydrogen | Nitrogen | Oxygen | |
| Ambient | 75.60 | 6.12 | 2.35 | 15.93 | 1.00 |
| 150 | 76.08 | 5.81 | 2.02 | 16.09 | .994 |
| 200 | 76.98 | 5.82 | 1.72 | 15.48 | .979 |
| 300 | 77.14 | 5.60 | .78 | 16.48 | .966 |
| 400 | 78.45 | 5.42 | .42 | 15.71 | .930 |
| 450 | 79.40 | 5.36 | .40 | 14.84 | .902 |
| 500 | 81.53 | 4.89 | | 13.58 | .855 |
| 550 | 84.22 | 4.47 | | 11.31 | .80 |
| 600 | 88.00 | 3.59 | | 8.41 | .73 |
| 650 | 90.81 | 2.85 | | 6.35 | .68 |
| 750 | 92.31 | 1.54 | | 6.15 | .59 |
| 850 | 92.65 | .90 | | 6.45 | .54 |

As these results show, the polymer was found to contain 75.60 percent carbon, 6.12 percent hydrogen, 2.35 percent nitrogen, and 15.93 percent oxygen. The percentage of nitrogen in the starting polymer is not surprising in view of the fact that ammonia NH_3 is a product of the decomposition of hexamethylenetetramine. Indication that this quantity of nitrogen is a trapped compound rather than an integral part of the polymer structure is shown in figure 9 where the elemental residual mass fraction is plotted as a function of decomposition temperature. The elemental residual mass fraction was obtained by converting the mass percentage for each element into absolute values. This conversion was possible through use of the residual mass fraction data obtained by mass loss measurement in the DTA apparatus, the results of which are shown in table II. The converted mass percentages (to absolute values) were then normalized with respect to the original mass of each element. The elemental residual mass fraction of nitrogen is seen to decrease drastically with a slight increase in temperature; thus, a nitrogen-containing compound had been trapped. The difference found between the experimental analysis shown in table II and the theoretical analysis of the assumed structure shown previously also lends support for the existence of trapped compounds within the polymer.

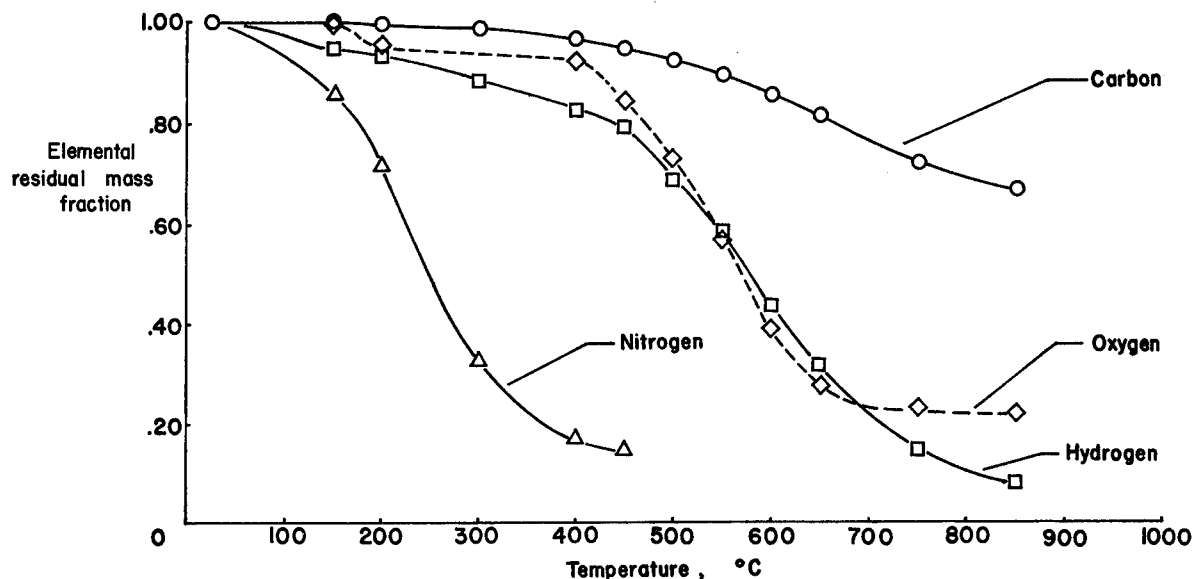


Figure 9.- Elemental residual mass fraction for decomposition of phenolic.

The second peak immediately observable on the DTA thermogram (fig. 4) is the exothermal range between 175° C and 350° C. This exotherm is seen to peak at approximately 265° C and involves 68 kJ/kg of original material. Gas analysis by gas chromatography in this temperature range identified water as the major product associated with this reaction, as shown in figure 6. Twenty-five percent by weight of the total quantity of water evolved is observed over this 175° C to 350° C range. The thermal characteristics of the material when heated through this temperature range thus indicate that the polymer is undergoing further curing and is eliminating the water produced by further condensation. The elemental analysis data in figure 9 also exhibit the loss of water by showing a loss in the elements hydrogen and oxygen through this temperature range.

Beyond 370° C, on the DTA thermogram (fig. 4), the basic character of the reactions becomes endothermic and any increase in temperature beyond this point is accompanied by the release of volatile products indicative of thermal breakdown of the polymer. An endothermic reaction is seen to peak at approximately 450° C which coincides with the maximum point in the evolution curve of water on figure 6. This maximum peak of water also marks the onset of production of carbon monoxide, hydrogen, and methane. With the increase from 380° C of the water component (fig. 6), large quantities of phenol and xylenol were also observed (fig. 7), and clearly indicate that the thermal breakdown of the polymer at the methylene bridge follows the initial breakdown at the -OH groups. The initial decomposition of the polymer is therefore observed as a depolymerization process at the lower decomposition temperatures.

After approximately 530° C, the endothermic character of the decomposition thermogram from the DTA indicates a second reaction or process to be in progress. The peak of this reaction is found to be at 625° C (fig. 4). The volatile products of this decomposition reaction, shown in table I, consist of carbon monoxide, hydrogen, methane, phenol, xylenol, and smaller quantities of carbon dioxide, benzene, toluene, and water. From this table and the evolution curves in figures 6 and 7, it is seen that the temperatures of maximum production of carbon monoxide, methane, and carbon dioxide nearly coincide with the peak of the reaction at 625° C on the DTA thermogram.

The elemental residual mass fractions of carbon, hydrogen, and oxygen are seen to decrease after 400° C (fig. 9), corresponding to the decomposition of the polymer shown in the DTA thermogram (fig. 4), and the observation of volatile products (table I). The elemental residual mass loss of oxygen (fig. 9) shows a marked decrease over this range corresponding to volatile decomposition products, such as carbon monoxide and carbon dioxide. The actual composition of the residue and char for a 100-gram specimen is shown in figure 10, where the composition in moles is shown as a function of temperature. These data show that between 400° C and 850° C, there is a loss of 1.9 moles of carbon, 4.6 moles of hydrogen, and 0.7 mole of oxygen. It is therefore observed that the 100-gram specimen of polymer incurred a loss of 7.2 moles between 400° C and 850° C.

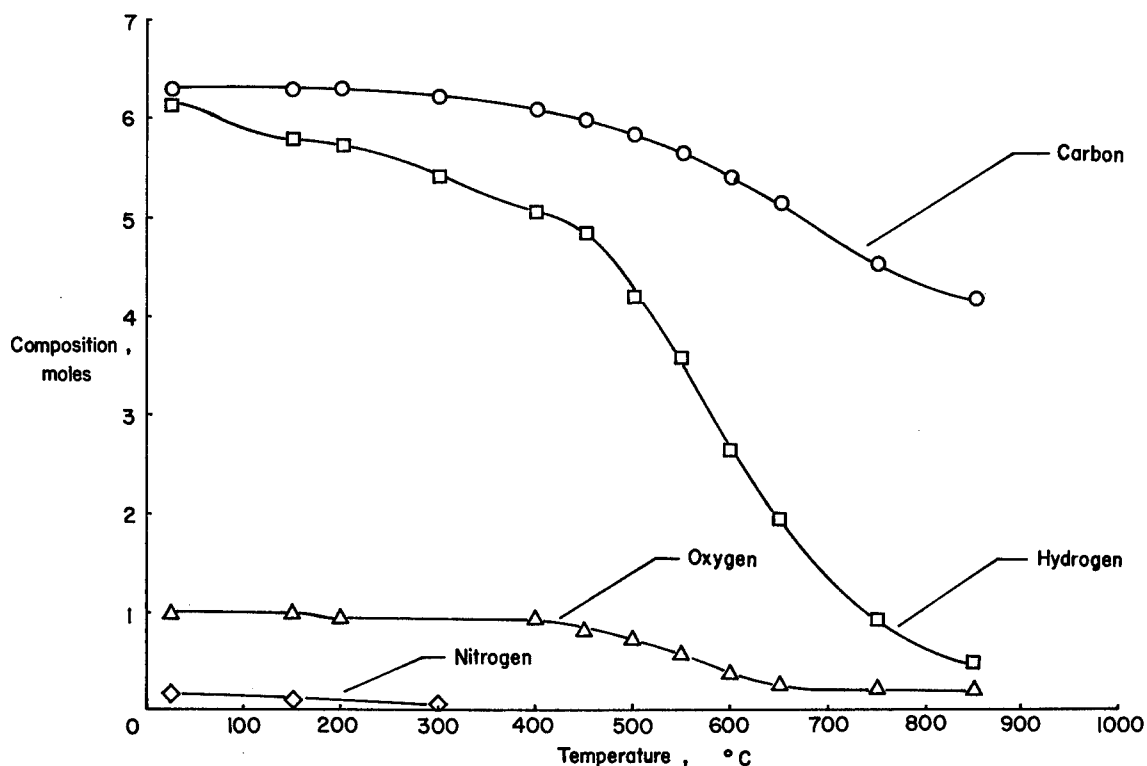


Figure 10.- Elemental composition for residue and char from decomposition of phenolic (100-gram specimen).

This loss is accounted for by the observation of volatile decomposition products, many of which were identified by gas chromatography through this temperature range.

The character of the DTA thermogram (fig. 4) after the final decomposition reaction at 625° C is a result of the drastic change in heat capacity which occurred in the polymer during the reaction. The effect of this change upon the DTA thermogram (fig. 4) is to shift the base line ($\Delta T = 0$) in the exothermal direction, and thus indicate the reaction to be complete at a lower temperature than is actually the case. The EGA thermogram, however, shows the actual characteristics of the final reaction. In figure 5 the gaseous products from the reaction are seen to continue to evolve through 900° C, where the major volatile product is hydrogen. The temperature of maximum production of hydrogen was the highest of those of the gases produced (fig. 6). The evolution of hydrogen through this range is also shown in the loss of this element, in the residue and char, as shown in the elemental analysis data in figure 9.

Discussion of Results

The principal changes observed upon heating phenolic from ambient to 350° C were seen to involve the release of large quantities of water. The water apparently stems from the release of occluded water at low temperatures and from continued crosslinking (curing) at temperatures approximating 250° C as evidenced by the exothermal condensation reaction on the DTA thermogram. This observation is consistent with the results of elemental analysis of the starting polymer which showed that a nitrogen compound had also been trapped during the molding procedure. At higher temperature, 350° C to 450° C, the water evolved was a direct result of thermal breakdown at the -OH groups attached to the ring structure of the polymer. This observation is substantiated by the increase in production of water and the endothermic character of the DTA thermogram observed through this temperature range. Water was observed to 700° C and accounted for 23.4 percent of the total moles identified. The total quantity of water evolved upon heating the polymer to decomposition temperatures therefore depends upon the degree of cure which the material has obtained prior to heating. The relatively large quantity of water identified agrees well with data obtained in reference 13, where 29 percent of total moles of the degradation products for a resole phenolic resin were found to be water.

The decomposition of the polymer therefore is shown to begin with breakdown at the -OH groups followed by a depolymerization process from which phenol and xylenol are the major products. Decomposition thus begins as early as 350° C and continues through 900° C where the major volatile product is hydrogen. Although the major early decomposition products were phenol and xylenol, the temperature of maximum production of water at 450° C marks the observation of several oxidized species, which, in turn, are not products of a depolymerization process. For example, carbon monoxide and carbon

dioxide were identified in appreciable quantities. Since the entire decomposition occurred in a nonoxidizing atmosphere, the oxygen source for these species must result from a source within the polymer. Such an oxygen source results from breakdown at the -OH groups, the water from which was identified through this range. It is apparent then that through the temperature range, 350° C to 900° C, products from thermal decomposition as well as those from oxidation are present. This result indicates that the observed decomposition of the polymer actually consists of two competing reactions occurring simultaneously, one a depolymerization and the other an oxidation. DTA results further showed that the resultant of these processes was endothermic in nature.

Examination of the decomposition products of a resole-type phenolic resin enabled the investigators of references 4 and 5 to postulate a mechanism for decomposition of their laboratory produced material. Their suggested mechanism included oxidation as well as thermal decomposition and the corresponding products from each. Comparison of the products of decomposition from the resole material (refs. 4 and 5) and the novolac material of this investigation indicates considerable similarity between the modes of decomposition of the two materials.

The decomposition of the polymer was shown by gas analysis to continue to 1000° C, where the major product of the reaction was hydrogen. Approximately 50.1 percent of the total moles identified were hydrogen and the temperature of maximum production of this product was the highest of those of the gases produced. Although the formation of such large quantities of hydrogen cannot be supported by the mechanism of decomposition outlined in references 4 and 5, other investigators have obtained quantities which agree well with those of the present investigation. The production of hydrogen by decomposition of phenol-formaldehyde polymers in references 13 and 14, produced 47 percent and 54 percent of the total moles, respectively.

The quantity of heat absorbed by endothermic decomposition of the polymer was determined to be 293 kJ/kg over the temperature range from 370° C to 750° C. The most important aspect of the decomposition of the polymer, however, is the formation of a carbonaceous residue through this endothermic process. The carbonaceous residue, 92.6 percent carbon, 0.9 percent hydrogen, and 6.5 percent oxygen at 850° C, is a result of the oxidative decomposition process occurring through the decomposition zone. Therefore, the appearance of oxidized species such as carbon monoxide also marks the formation of carbon char. Carbon monoxide appeared as a volatile product in appreciable quantities between 450° C and 850° C and its temperature of maximum production was observed at 625° C. The char-forming reaction is therefore found to correspond to the last major endothermic processes also at 625° C on the DTA thermogram. This conclusion is substantiated by the results of elemental analysis after 450° C. The elemental residual mass fraction of oxygen is seen to decrease drastically through this temperature

range; this fraction corresponds to the loss of oxygen in the polymer and the observance of oxidized species, such as carbon monoxide and carbon dioxide, as volatile products. The elemental analysis data for carbon also reflect this change by going from 79.4 percent carbon at 450° C to 92.6 percent carbon at 850° C. A 100-gram specimen of polymer heated to this temperature would therefore contain 4.16 moles of carbon, 0.48 mole of hydrogen, and 0.21 mole of oxygen.

The decomposition of the polymer has been shown to be composed of several complex reactions occurring over the temperature range from 350° C to 850° C. The decomposition zone or pyrolysis zone was shown by DTA results to absorb 293 kJ/kg through this 350° C to 850° C temperature range. The decomposition zone width would also exist in composite heat-shield form (no interaction between components being assumed). However, if the pyrolysis zone is defined as the zone of greatest mass loss, gas evolution, and heat absorption through decomposition, obviously, an added component, such as nylon as in the case of references 1, 2, and 3 or other similar material, would determine the pyrolysis zone and characteristics of the same while in heat-shield form. Such a material as nylon would be added in order that large volumes of gas would be generated upon decomposition for boundary-layer injection; the energy absorption by decomposition would be large and the polymer would decompose completely, and thus have essentially a 100-percent loss in mass. Therefore, the pyrolysis zone of an ablation heat-shield specimen, which is composed of the phenolic of this investigation and other components such as the case in the aforementioned references, would be determined by the characteristics of decomposition of the major gas-producing component.

Other performance characteristics of the composite ablation material could, however, be greatly affected by the decomposition of the phenolic component. Ablation specimens of high open porosity, such as the low-density phenolic nylon specimen of reference 3, for example, could be notably susceptible to the type and quantity of decomposition products produced by decomposition in reentry. Products having the most effect would be products such as water, phenol, xylenol, and etc., which are condensable below pyrolysis zone temperatures. Such products were found to result from decomposition of the phenolic component and of these, water and phenol were the major products, being 23.4 percent and 7.1 percent of the total moles, respectively. A portion of the products evolving from the pyrolysis zone could be forced, as a result of reentry conditions and the high porosity of the material, to the unpyrolyzed material behind the pyrolysis zone. From this condition it would then be expected that products such as water, phenol, xylenol, and etc., would condense on this material. As the pyrolysis zone and decomposition progress through the unpyrolyzed material, the temperature of the material behind the pyrolysis zone would remain isothermal, the temperature corresponding to the heat absorption by vaporization of the condensed products, until the products were completely vaporized.

CONCLUSIONS

The decomposition of the phenolic ablation component, characterized by several analytical techniques, has led to the following conclusions:

1. The major product identified from heating phenolic at low temperatures was water; this result indicated considerable entrapment during molding and insufficient curing.
2. The actual decomposition reactions of the polymer, observed between 350° C and 1000° C, were found to be endothermic and absorbed 293 kJ/kg.
3. The major decomposition products were hydrogen (50.1 percent of total moles), water (23.4 percent), methane (10 percent), phenol (7.1 percent), carbon monoxide (5.5 percent), and xylenol (1.8 percent).
4. The char, 92.6 percent carbon, 0.9 percent hydrogen, and 6.4 percent oxygen at 850° C, was found over the temperature range between 450° C and 850° C.

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